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Test Report T68-7-1

APPLICATION OF INFRARED SPECTROSCOPY TO THE ANALYSIS  
OF INORGANIC NITRATES

Phase I: Spectra of Inorganic Nitrates in Acetone  
and the Use of Such Spectra in Analytical  
Chemistry

by

George Norwitz  
David E. Chasan

May 1968

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## 1. SUMMARY

A study was made of the spectra of soluble inorganic nitrates in acetone solution and the use of such spectra in analytical chemistry. The following inorganic nitrates were studied:  $\text{LiNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Y}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ ,  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{ZrO}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ . The spectra of the soluble nitrates indicate the nitrate peaks in acetone can best be accommodated by a  $\text{C}_{2v}$  point group assignment and the nitrate groups in the nitrate acetone system are essentially covalent in character. As judged by the difference between the pair of  $\text{NO}_2$  stretches,  $\nu_4$  and  $\nu_1$ , the compounds tested could be classified into four groups: group 1 consisting of  $\text{LiNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2$ , and  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  which exhibited the least covalent characteristics; group 2 consisting of  $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , and  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  which showed a higher degree of covalency than group 1; group 3 consisting of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Y}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$  which showed a higher degree of covalency than group 2; group 4 consisting of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ , and  $\text{ZrO}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$  which showed the highest degree of covalency of all the compounds tested.

Water of hydration (or added water) did not change the position of the nitrate peaks but it did have the effect of producing an additional broad peak at  $3500\text{ cm}^{-1}$  and lowering the base line at about  $1650\text{ cm}^{-1}$  and between  $800$  and  $650\text{ cm}^{-1}$ .

The effect of nitrate on the acetone peaks is briefly discussed.

A study was made of the solubilities of anhydrous inorganic nitrates in acetone.

The applications of the spectra of inorganic nitrates in acetone to analytical chemistry is discussed. A method is proposed for the determination of calcium in the presence of strontium or barium by treating the nitrates with acetone, filtering off the insoluble strontium or barium nitrates, and measuring the nitrate peak from the calcium nitrate at  $824\text{ cm}^{-1}$ . A similar procedure is also recommended for the determination of lithium in the presence of strontium and barium.

## II. RECOMMENDATIONS

It is recommended that the spectra of inorganic nitrates and methods for calcium and lithium be included in appropriate military documents and specifications. It is also recommended that the investigation of the application of infrared spectroscopy to the analysis of inorganic nitrates by various techniques be continued.

## III. INTRODUCTION

Apparently, little has been reported in the literature on the infrared spectra of inorganic nitrates in acetone. Slovokhotova (16) in investigating the nature of inorganic salt solutions in ketones, considered the spectrum of  $\text{Ca}(\text{NO}_3)_2$  in acetone. Fogg (7) makes mention of the spectrum of  $\text{Ca}(\text{NO}_3)_2$  in acetone. Ryskin (14) briefly mentions the spectrum obtained for  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in methyl ethyl ketone.

This laboratory undertook an investigation of the infrared spectra of various inorganic nitrates in acetone and the possible application of such spectra to the solution of some analytical problems.

## IV. STUDY

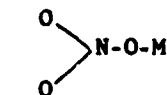
### A. CHEMISTRY AND STRUCTURE OF INORGANIC NITRATES

Certain aspects of the chemistry and structure of inorganic nitrates have considerable bearing on this study. These aspects will be discussed briefly.

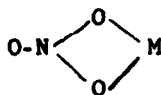
Inorganic nitrates can be divided into two classes: ionic nitrates and covalent nitrates.

In ionic nitrates the nitrate group is electrostatically bonded to the metal. The formula of an anhydrous nitrate can be represented as  $\text{M}^+\text{NO}_3^-$ .

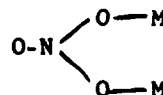
In covalent nitrates the nitrate group is covalently bonded through one, two, or bridging oxygen atoms. These types of bonding can be illustrated as follows:



Monodentate



Bidentate



Bridging

The nitrate ion has a configuration of an equilateral triangle with three planar N-O bonds and a group  $D_{3h}$  symmetry (9).

Nitrate in the covalent state has a group  $C_{2v}$  symmetry (1) whether monodentate, bidentate, or bridging.

The four fundamental frequencies of the nitrate ion ( $\nu_1$ ,  $\nu_2$ ,  $\nu_3$  and  $\nu_4$ ) as calculated by Herzberg (9) are shown in Table I.

Nitrate in the covalent state has six fundamental frequencies ( $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ ,  $\nu_4$ ,  $\nu_5$ , and  $\nu_6$ ). The values of these frequencies as reported by Gatehouse, Livingstone, and Nyholm (8) are shown in Table II.

The following are considered to be ionic nitrates: anhydrous nitrates of lithium, sodium, potassium, rubidium, cesium, calcium, magnesium, strontium, barium, lead, and silver; hydrated nitrates of cadmium, cobalt, copper, iron (III), nickel, and zinc.

The following are considered to be covalent nitrates: anhydrous aluminum, beryllium, and the heavy metal nitrates; the rare earth nitrates; anhydrous ceric ammonium nitrates; hydrated thorium, zirconyl, and uranyl nitrates.

The exact structure (monodentate, bidentate, or bridging) of the above covalent compounds is in most instances uncertain. Ceric ammonium nitrate is considered to be monodentate, tin and titanium nitrates are considered to be bidentate, and thorium and uranyl nitrates are considered to have bridging structures.

Inorganic nitrates can be conveniently divided by their anhydrous character into three groups: (a) those that are obtainable commercially as anhydrous nitrates (ammonium, barium, cesium, lead, lithium, potassium, rubidium, silver, sodium, strontium, and thallous nitrates); (b) those that can be readily obtained as anhydrous nitrates by heating the commercial hydrates (calcium nitrate); and (c) those that can only be prepared in the anhydrous state by special means, for instance, by reactions involving  $N_2O_4$ ,  $N_2O_5$ , or  $ClNO_3$  in a non-aqueous medium; when the hydrates of these nitrates are heated some hydrolysis and loss of  $HNO_3$  takes place (some examples of these nitrates are aluminum, beryllium, magnesium, manganese, uranyl, and heavy metal nitrates (1, 6, 11)).

## B. SOLUBILITY OF INORGANIC NITRATES IN ACETONE

In the first experimental work in this project, the solubilities of the common anhydrous nitrates in acetone were established. For this study, the following salts (highest purity) were ground in a mortar and dried at 130° C. for 3 hours:  $\text{NH}_4\text{NO}_3$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{CaNO}_3$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{LiNO}_3$ ,  $\text{KNO}_3$ ,  $\text{RbNO}_3$ ,  $\text{AgNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{Sr}(\text{NO}_3)_2$ , and  $\text{TlNO}_3$ . Anhydrous  $\text{Ca}(\text{NO}_3)_2$  was prepared by heating  $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  on the hot plate at gentle heat until most of the water had been driven off (this salt dissolves in its own melt) and then drying at 170° C. for 6 hours. All the salts were stored in a desiccator containing Anhydron.

Preliminary tests established that calcium and lithium nitrates were very soluble while the other anhydrous nitrates were only slightly soluble or insoluble. It was found that different techniques had to be used to establish the exact solubilities of the soluble and slightly soluble salts.

Saturated solutions of the nitrates in acetone were prepared by shaking an excess of the high purity salts with acetone (ACS Grade, Fisher Scientific Co.) overnight in glass stoppered flasks at 25° C. For the calcium and lithium nitrates approximately 100 ml of acetone contained in 125-ml glass-stoppered flasks were used; for the other nitrates approximately 250-ml of acetone contained in 250-ml glass stoppered flasks were used. For the calcium nitrate and lithium nitrate approximately 10 and 50-ml aliquots, respectively, of the supernatant liquid (at 25° C.) were pipetted into tared 50-ml glass-stoppered flasks and the flasks were weighed to obtain the weights of the solutions. The solutions were evaporated to dryness on the steam bath, the salts were heated at 170° C. for 3 hours, and the flasks were weighed again to obtain the weights of the salts. For the other nitrates approximately 200-ml aliquots (at 25° C.) were pipetted into tared 250-ml glass-stoppered flasks, the flasks were weighed to obtain the weights of the solutions, and the solutions were then filtered through sintered glass crucibles of fine porosity (to eliminate any particles of undissolved salts). The solutions were then transferred in portions to tared 50-ml glass-stoppered flasks, the acetone was evaporated off, the salts were dried at 130° C. for 3 hours, and the flasks were weighed again to obtain the weights of the salts.

A blank was carried through the procedure using the same volume of acetone as was used in the method.

The results obtained for the solubilities (grams of salt per 100 grams of solution) are shown in Table III.



Ceric ammonium nitrate (anhydrous) was found to be moderately soluble in acetone. However, the exact solubility was not determined since it is known that evaporation of an acetone solution containing Ce (IV) (a powerful oxidizing agent) to dryness after taking the aliquot would be hazardous.

Apparently the solubilities in acetone of most of the salts shown in Table I have not been previously determined. Bell, Rowlands, Bamford, Thomas, and Jones (3) give the solubility of  $\text{Ca}(\text{NO}_3)_2$  as 16.8 grams per 100 grams of solution at 20° C., while D'Ans and Siegler (4) give the solubility of this salt as 58.5 grams per 100 grams of acetone at 25° C. D'Ans and Siegler (4) give the solubility of  $\text{Sr}(\text{NO}_3)_2$  as 0.02 gram per 100 grams of acetone at 25° C. It is believed here that the solubility data of D'Ans and Siegler (4) is in error, possibly because of presence of water in the acetone or the use of impure salts. The latter may be a point that is overlooked. In experiments with the solubility of barium nitrate in this laboratory, initially ordinary reagent grade barium nitrate was used and a fairly significant amount of residue was obtained after the evaporation. Spectrographic examination of the residue, however, showed that it consisted of mostly calcium and sodium and very little barium. When the experiment was repeated using the highest purity barium nitrate obtainable ("Specpure", Johnson, Matthey and Co., London, England) the low result shown in Table I was obtained.

No quantitative tests were conducted on the solubilities of hydrated inorganic nitrates since it is not usually possible to evaporate the acetone from the hydrated salts and obtain the anhydrous salts without the decomposition mentioned earlier. The presence of water from the water of hydration makes interpretation of the results difficult. Qualitative tests, however, were conducted and it was found that the hydrates of calcium, cobalt, cadmium, lanthanum, cerium, magnesium, manganese, nickel, thorium, uranyl, and zinc nitrates were very soluble while the hydrates of thorium, zirconyl, and copper nitrates were moderately soluble and the hydrates of aluminum, chromium, ferric, mercurous, and mercuric nitrates were only very slightly soluble.

It was found that significant spectra of inorganic nitrates in acetone could only be obtained for salts that were at least moderately soluble in acetone. This was not unexpected since it is not ordinarily feasible to determine the infrared spectra of small concentrations of materials using the solution technique. This is principally due to the relatively small thickness cells that must be used in order to keep the absorption of the solvent to a satisfactory minimum. In addition, most organic compounds exhibit absorption bands in the 1500-1000  $\text{cm}^{-1}$  region which interfere with the nitrate. Specifically, the strong broad acetone bands at about 1400  $\text{cm}^{-1}$  interfere to some extent with the strongest nitrate peak.

## C. SPECTRA OF INORGANIC NITRATES IN ACETONE

### 1. Experimental Work for Obtaining the Spectra

The spectra obtained for the following inorganic nitrates in acetone were determined:  $\text{LiNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Y}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ ,  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{ZrO}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ .

A Perkin-Elmer 621 Infrared Spectrophotometer was used. Spectra were obtained for all the compounds using an Irtran-2 cell of 0.028mm thickness. These spectra are shown in Figures 1 to 17. The spectrum of acetone using this cell is shown in Figure 18.

Some experimental work was carried out on the spectra of calcium nitrate and lithium nitrate using sodium chloride cells. This type of cell could not be used for the heavy metal nitrates because of attack of the cell.

### 2. Nitrate Peaks in Acetone

The nitrate peaks observed in acetone solution are listed in Table IV. The observed frequencies fall into the following ranges: 730-763  $\text{cm}^{-1}$ , 804-827  $\text{cm}^{-1}$ , 1003-1042  $\text{cm}^{-1}$ , 1278-1325  $\text{cm}^{-1}$ , and 1455-1562  $\text{cm}^{-1}$ . In a few cases more than one peak is observed within these ranges as some sort of splitting takes place. It should be pointed out that in some instances assignment of the exact frequencies of peaks is complicated by interferences from solvent peaks. Also, the intensity values are difficult to assign because of the complications of solvent interference, coupling, and broadening.

It is seen from a comparison of Tables I, II, and IV that the nitrate peaks observed in acetone can best be accommodated by a  $\text{C}_{2v}$  point group assignment. This would indicate the presence of covalent nitrate groups in most of the nitrate-acetone systems studied. These results are consistent with those of previous organic solution studies.

Katzin (10), for example, pointed out that in tributyl phosphate solutions a definite covalent bond is formed between the anion and the metallic cation. Even with conventionally ionic crystals, the interaction in solution is sufficient to modify the vibrational pattern to that of the covalently bound ligand.

The distance between the pair of  $\text{NO}_2$  stretches,  $\nu_4$  and  $\nu_1$ , is related to the tendency of the metal to share electrons with the nitrate ion in the solvent under consideration (i.e. as a measure of degree of covalent bond character), (2, 10, 19). The values for this splitting,  $\Delta\nu$ , in acetone, tributyl phosphate and tri-n-octyl phosphine oxide in carbon tetrachloride are shown in Table V. The values for  $\Delta\nu$  as well as the positions of the nitrate bands in acetone show remarkable agreement in most cases, with those in tributyl phosphate and tri-n-octyl phosphine oxide in carbon tetrachloride solution.

There seem to be four general groupings with respect to the degree of splitting in acetone:

1. The spectra of  $\text{LiNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2$ , and  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  exhibit the least covalent characteristics of all the nitrates that are soluble in acetone. Katzin (10) set an approximate  $\Delta\nu$  value of  $100 \text{ cm}^{-1}$  as the boundary between spectra due to covalently bonded and electrostatically bonded nitrates. This would place lithium nitrate ( $\Delta\nu = 80 \text{ cm}^{-1}$ ) on the electrostatic side. Magnesium nitrate ( $\Delta\nu = 90 \text{ cm}^{-1}$ ) and calcium nitrate ( $\Delta\nu = 100 \text{ cm}^{-1}$ ) would be borderline cases. In each of these spectra, the  $\nu_4$  peak is seen only as a shoulder on the right side of the acetone peak at  $1420 \text{ cm}^{-1}$ .

2.  $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , and  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  exhibit a higher degree of covalency. The  $\Delta\nu$  values fall between  $160$ - $180 \text{ cm}^{-1}$ , well over the  $100 \text{ cm}^{-1}$  criteria necessary for covalent bonding. The  $\nu_4$  peak appears as a shoulder on the left side of the  $1420 \text{ cm}^{-1}$  acetone peak.

3.  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Y}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$  have  $\Delta\nu$  values ranging from  $202$ - $213 \text{ cm}^{-1}$ . These values seem to indicate an even higher degree of covalency in these metal to nitrate bonds. In each case the  $\nu_4$  nitrate peak now appears as a distinct, separate peak to the left of the  $1420 \text{ cm}^{-1}$  acetone peak.

4.  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  have  $\Delta v$  values in acetone of 249 and 235  $\text{cm}^{-1}$ , respectively, indicating the presence of very strong covalent bonds. This would coincide with the bridging structures that have been postulated for those compounds (5). Bac (2), in fact, suggests such a relationship as an explanation for the large  $\Delta v$  value for  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  in KBr. The high  $\Delta v$  value of 279  $\text{cm}^{-1}$  for  $\text{ZrO}(\text{NO}_2)_3 \cdot 4\text{H}_2\text{O}$  suggests that it too, contains bridging structures.

The use of acetone instead of tributyl phosphate or tri-n-octyl-phosphine oxide permits viewing of the N-O stretch at approximately 1030  $\text{cm}^{-1}$ . The strong P-O band found in tributyl phosphate and tri-n-octyl-phosphine oxide at approximately 1000  $\text{cm}^{-1}$  does not allow any measurement of nitrate peaks in this region with these solvents. For each nitrate in acetone solution, a weak to medium sharp band was observed in this region.

The appearance of a second band in this region (about 1030  $\text{cm}^{-1}$ ) for  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is unusual for infrared studies. It has been observed in Raman work (12) with a quite prominent second peak observed in solutions of copper nitrate. No significance has yet been attached to this splitting.

### 3. Effect of Water on the Spectra

The effect of water on the spectra of nitrates in acetone was investigated. In this study a comparison was made of the following spectra: water using an Irtran-2 cell (figure 19),  $\text{Ca}(\text{NO}_3)_2$  dried at 170° C. using a 0.189 mm sodium chloride cell (figure 20), and  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  using a 0.189 mm sodium chloride cell (figure 21).

The following conclusions were made concerning the effect of water:

1. Water does not change the position of the nitrate peaks.
2. Water causes the introduction of a broad peak at about 3500  $\text{cm}^{-1}$ . The intensity of this peak increases as the amount of water increases.
3. Water causes a lowering of the base-line in the regions of about 1650  $\text{cm}^{-1}$  and between 800 and 650  $\text{cm}^{-1}$ .

Only the last effect presents any real interference problem in viewing the nitrate spectra and in a few cases the spectra cannot be observed at a frequency lower than 750  $\text{cm}^{-1}$ . The Irtran-2 cell itself begins to absorb around 800  $\text{cm}^{-1}$  so this region is of limited value in any case.

#### 4. Effect of Nitrates on Acetone Peaks

This project was not primarily concerned with the effect of the inorganic nitrates on the acetone spectrum. However, the topic was examined since it was of interest and involved no additional experimental work.

As previously stated, the spectrum of acetone is shown in figure 18. The intensity, and assignments for the principal bands are shown in Table VI.

The presence of the nitrate has the following effect on the acetone peaks:

1. The shape of the band at  $1715\text{ cm}^{-1}$  is very slightly altered. It seems to break into a few components in the spectra of  $\text{LiNO}_3$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ , and  $\text{ZrO}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ . Fogg (7), in his study of complex formation in acetone, also notes this effect in acetone solutions of  $\text{Ca}(\text{NO}_3)_2$  and attributes it to the formation of acetone complexes. Later studies of other nitrate-organic solvent systems (10, 19) showed a nitrate combination peak appearing at approximately  $1720\text{ cm}^{-1}$ . The presence of this peak is probably the cause of the apparent multiplicity of this acetone peak.

2. The  $1220\text{ cm}^{-1}$  acetone band also develops a definite, but less noticeable multiplicity in the nitrate solutions. It is most evident in the spectra of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{ZrO}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ .

#### D. QUANTITATIVE DETERMINATION OF CALCIUM NITRATE IN ACETONE SOLUTION; DETERMINATION OF CALCIUM IN THE PRESENCE OF STRONTIUM AND BARIUM

Attention was next focused on the use of the spectra of inorganic nitrates in acetone for quantitative analysis. The insoluble inorganic nitrates obviously cannot be analyzed by this technique. The hydrated salts of the soluble inorganic nitrates cannot be analyzed accurately because of the effect of water in causing a sloping base-line. The most useful application of the technique was the determination of calcium and lithium nitrates.

The method for calcium nitrate was applied to the determination of calcium in the presence of strontium and barium, after first extracting calcium nitrate from the strontium and barium nitrates. The latter two salts are practically insoluble in acetone as can be seen from Table III.

Calcium in the presence of strontium has been determined by previous investigators by separating calcium nitrate from strontium nitrate by use of acetone and determining the calcium gravimetrically (15, 17, 18). Apparently, acetone has not been used for the separation of calcium nitrate from barium nitrate.

It is proposed that calcium nitrate be separated from strontium and barium nitrates by use of acetone and the calcium nitrate then be determined in the filtrate by infrared using the sharp symmetrical nitrate peak at  $824\text{ cm}^{-1}$  and a 0.4-mm sodium chloride cell. Before making the infrared measurement the solution is evaporated to about 2 ml with a stream of air and is then diluted to 5 ml in a volumetric flask. Since the presence of moisture in the acetone causes a low-base-line and somewhat erratic results, it is essential that the air used in the evaporation be dry and that the evaporation be conducted in a dry box. If the evaporation is conducted without a dry box, the moisture of the air condenses around the top of the beaker because of the cooling effect of the vaporization. The difficulties caused by moisture preclude the use of a steam bath or water bath as a means for hastening the evaporation.

The recommended range of the method is 0.001 to 0.08 gram of calcium nitrate in the presence of up to about 0.2 gram of barium or strontium nitrate.

#### Reagents

Acetone, reagent grade, ACS specification.

Anhydrous calcium nitrate. Heat  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in a weighing dish on the hot plate at gentle heat until most of the water is driven off, then heat in an oven at  $170^\circ\text{C}$ . for 6 hours, cover, and store in a desiccator containing Anhydron.

Standard calcium nitrate solution. Weigh to 0.1 mg approximately 1.0 gram of anhydrous calcium nitrate, dissolve in acetone, and dilute to 50 ml in a volumetric flask with acetone.

#### Preparation of Calibration Curves

Transfer 1.00, 2.00, 3.00, and 4.00 ml portions of the standard calcium nitrate solution into four 5-ml volumetric flasks and dilute to the mark with acetone. Obtain the spectrum from  $860\text{ cm}^{-1}$  to  $800\text{ cm}^{-1}$  using a 0.4-mm sodium chloride cell. (The following settings were used on a Perkin-Elmer Model 621 infrared spectrophotometer: slit program, 1000; gain, 5.3; attenuator speed, 1100; scan time, 64;

suppression, 0; scale, 1X; source current, 0.8). Determine the absorbance of the peak at  $824\text{ cm}^{-1}$  by the base-line technique and plot absorbance against grams of calcium nitrate in the 5-ml volume.

#### Method

The calcium, strontium, and barium must be in the form of nitrates. Oxides and carbonates can be converted to nitrates by treating in a 50-ml beaker with 1 to 1 nitric acid, evaporating to dryness on the hot plate, washing down the sides with water, and again evaporating to dryness. Oxalates cannot be converted to nitrates by treatment with nitric acid; it is first necessary to convert them to oxides by ignition and then treat the oxides with nitric acid.

Dry the sample containing up to 0.08 gram of calcium nitrate and up to about 0.2 gram of strontium or barium nitrate (in a 50-ml beaker) by heating in an oven at  $170^{\circ}\text{C}$ . for 1 to 3 hours (depending on the amount of salt present). Cool in desiccator containing Anhydrone. Add 20 ml of acetone, break up any clumps by use of a policeman, wash down the policeman with a little acetone, and remove it. Insert a small stirring rod and allow to stand for 2 hours with occasional stirring. Filter through a sintered glass crucible of fine porosity (this crucible should be tared if strontium or barium is to be determined). Transfer the precipitate to the crucible and wash the crucible several times with acetone.

If the determination of strontium or barium is desired, dry this crucible at  $130^{\circ}\text{C}$ . for 1 hour, cool in a desiccator, and weigh the  $\text{Sr}(\text{NO}_3)_2$  or  $\text{Ba}(\text{NO}_3)_2$ . Calculate the percent strontium or barium in the sample (the factors for converting  $\text{Sr}(\text{NO}_3)_2$  to Sr, and  $\text{Ba}(\text{NO}_3)_2$  to Ba are 0.4140 and 0.5255, respectively).

Evaporate the filtrate to a volume of about 2 ml with a stream of air that has been dried by passing it through Anhydrone. During the evaporation the beaker must be protected from the atmosphere by the use of a dry box. (The dry box used in this laboratory consisted of a cardboard box and top approximately  $10 \times 6 \times 4$  inches, containing about a half-inch layer of Drierite. A platform for holding the beakers was placed on top of the Drierite. The platform consisted of a piece of cardboard containing about one perforation ( $1/4$  inch in diameter) per square inch. Two holes to be used as inlets for the dry air streams were made in the top of the box directly over the position of the beakers.)

Immediately after the evaporation, wash the solution from the beaker into a 5-ml volumetric flask with acetone and dilute to the mark with acetone.

Obtain the spectrum as described under preparation of calibration curve.

Determine the grams of calcium nitrate by reference to the calibration curve for calcium nitrate. Calculate the percent calcium (the factor for converting  $\text{Ca}(\text{NO}_3)_2$  to Ca is 0.2442).

### Results

The results obtained for calcium, strontium, and barium nitrates in synthetic mixtures are shown in Table VII.

#### E. QUANTITATIVE DETERMINATION OF LITHIUM NITRATE IN ACETONE SOLUTION; DETERMINATION OF LITHIUM IN THE PRESENCE OF STRONTIUM AND BARIUM

Lithium nitrate can be determined by measuring the peak at  $827\text{ cm}^{-1}$ .

The recommended range of the method is 0.001 to 0.08 gram of lithium nitrate in the presence of about 0.2 gram of strontium or barium nitrate.

The procedure for the determination of lithium in the presence of strontium and barium is as follows.

### Reagents

Acetone, reagent grade, ACS specification.

Anhydrous lithium nitrate. Dry reagent grade  $\text{LiNO}_3$  in an oven at  $170^\circ\text{C}$ . for 2 hours, and store in a desiccator containing Anhydrone.

Standard lithium nitrate solution. Weigh to 0.1 mg approximately 1.0 gram of anhydrous lithium nitrate, dissolve in acetone, and dilute to 50 ml in a volumetric flask with acetone.

### Preparation of Calibration Curve

Transfer 1.00, 2.00, 3.00, and 4.00 ml portions of the standard lithium nitrate solution into four 5-ml volumetric flasks and dilute to the mark with acetone. Measure the spectra at  $827\text{ cm}^{-1}$  as described for calcium nitrate and plot absorbance against grams of lithium nitrate in the 5-ml volume.



#### Method

The lithium, strontium, and barium must be in the form of nitrates.

Dry the sample containing up to 0.08 gram of lithium nitrate and up to about 0.2 gram of strontium or barium nitrate in a 50-ml beaker by heating in an oven at 170° C. for 1 hour. Cool in a desiccator containing Anhydron. Proceed with the extraction with acetone, evaporation, dilution to 5 ml, and measurement of the nitrate peak (at 827  $\text{cm}^{-1}$ ) as described for calcium.

Determine the grams of lithium nitrate by consulting the calibration curve for lithium nitrate. Calculate the percent lithium (the factor for converting  $\text{LiNO}_3$  to Li is 0.1007).

#### Results

The results obtained for lithium, strontium, and barium nitrates in synthetic mixtures are shown in Table VIII.

#### ACKNOWLEDGMENT

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## VI. TABLES

Table I. Fundamental Vibrations of the Nitrate Ion<sup>(9)</sup>

Type	$\nu_4$	$\nu_2$	$\nu_1^a$	$\nu_3$
Assignment	NO <sub>2</sub> bend (planar rock)	out-of-plane NO bend	stretch	NO <sub>2</sub> asymmetrical stretch
Frequency (cm <sup>-1</sup> )	720	831	1050	1390

<sup>a</sup> Infrared inactive

Table II. Fundamental Vibrations of the Covalent Nitrate Group<sup>(8)</sup>

Type	$\nu_5$	$\nu_3$	$\nu_6$	$\nu_2$	$\nu_1$	$\nu_4$
Assignment	NO <sub>2</sub> bend asymmetrical (out-of-plane) rock	NO <sub>2</sub> bend symmetrical	out-of-plane rock	NO stretch	NO <sub>2</sub> symmetrical stretch	NO <sub>2</sub> asymmetrical stretch
Frequency (cm <sup>-1</sup> )	~713	~739	781-800	970-1034	1253-1290	1481-1531

Table III. Solubilities of Common Anhydrous Inorganic Nitrates in Acetone at 25° C.

<u>Inorganic Nitrate</u>	<u>Solubility (grams per 100 grams of solution)</u>
NH <sub>4</sub> NO <sub>3</sub>	0.145
LiNO <sub>3</sub>	7.37
NaNO <sub>3</sub>	0.024
KNO <sub>3</sub>	0.015
CsNO <sub>3</sub>	0.0089
RbNO <sub>3</sub>	0.014
AgNO <sub>3</sub>	0.192
TlNO <sub>3</sub>	0.028
Ca(NO <sub>3</sub> ) <sub>2</sub>	33.08
Ba(NO <sub>3</sub> ) <sub>2</sub>	0.0002
Sr(NO <sub>3</sub> ) <sub>2</sub>	0.0002
Pb(NO <sub>3</sub> ) <sub>2</sub>	0.0062

Table IV. Observed Nitrate Peaks in Acetone

No.	Inorganic Nitrate	Position	Mature <sup>a</sup>	Intensity <sup>b</sup>	Position	Mature	Intensity	Position	Mature	Intensity	Position	Mature	Intensity	Position	Mature	Intensity
		(cm <sup>-1</sup> )			(cm <sup>-1</sup> )			(cm <sup>-1</sup> )			(cm <sup>-1</sup> )			(cm <sup>-1</sup> )		
1.	LiNO <sub>3</sub>	734	vv	sp	827	w	sp				1037	w	sp			
2.	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O				825	w	sp				1042	w	sp			
3.	Ca(NO <sub>3</sub> ) <sub>2</sub>	737	w	sp	824	w	sp				1032	w	sp			
4.	Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	737	w	sp	824	w	sp				1032	w	sp			
5.	Mn(NO <sub>3</sub> ) <sub>2</sub> ·xH <sub>2</sub> O				818	w	sp				1027	w	sp			
6.	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O				818	w	sp				1025	m	sp	1289	s	sp
7.	La(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	734	w	sp	818	w	sp				1028	m	sp	1298	s	sp
8.	Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	736	w	sp	820	m	sp				1032	m	sp	1300	s	sp
9.	(NH <sub>4</sub> ) <sub>2</sub> Ce(NO <sub>3</sub> ) <sub>6</sub>	730	w	sp	812	w	sp	(1003 vv sp)			1022	w	sp	1295	s	sp
10.	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O				811	w	sp	1014	m	sp				1286	s	sp
11.	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	756	w	sp	806	w	sp	1019	w	sp	1041	w	sp	1297	s	sp
12.	Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O				804	w	sp	1006	m	sp				1283	s	sp
13.	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	750	w	sp	806	w	sp	1018	m	sp				~1285	m	b
14.	Y(NO <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	745	w	sp	816	w	sp				1028	m	sp	1294	s	sp
15.	Th(NO <sub>3</sub> ) <sub>4</sub> ·4H <sub>2</sub> O	742	m	sp	810	m	sp				1025	m	sp	1290	s	sp
16.	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	747	w	sp	806	w	sp				1027	w	sp	1278	m	sp
17.	ZrO(NO <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	763	w	sp				1017	w	sp				1283	m	sp

<sup>a</sup> w = weak, m = medium, s = strong

<sup>b</sup> sp = sharp, b = broad, sh = shoulder

Table V. Values for  $\nu_4-\nu_1$  ( $\text{cm}^{-1}$ ) for Inorganic Nitrates in Three Solvents

No.	Compound	$\nu_4-\nu_1$ ( $\text{cm}^{-1}$ )		
		Acetone	Tributyl Phosphate (10)	Tri-n-Octyl Phosphine Oxide in $\text{CCl}_4$ (19)
1	$\text{LiNO}_3$	~80	65	
2	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	~90	90	
3	$\text{Ca}(\text{NO}_3)_2$	~106	127	
4	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	~106	127	
5	$\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	~160		
6	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	~171	170	156
7	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	~177	176	194
8	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	179	200	188
9	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	180		
10	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	202	210	206
11	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	~203	~213	
12	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	207	210	204
13	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	~210	~212	212
14	$\text{Y}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$	213		
15	$\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$	235	215	245
16	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	249	242	227
17	$\text{ZrO}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$	279		

Table VI. The Principal Infrared Peaks of Acetone

Position ( $\text{cm}^{-1}$ )	Nature	Intensity	Assignment (13)
785	sp <sup>a</sup>	w <sup>a</sup>	C-C stretching
903	sp	m	
1092	sp	s	
1215	sp	s	C-C antisym. stretching
1360	b	s	
1420	b	s	
1715	b	s	C = O stretching
2145	sp	w	
2305	b	w	
2440	sp	w	C = O stretching overtone
2570	sp	w	
2840	sh	w	
2920	sh	m	
2962	sh	m	
3005	vsp	s	
3411	sp	m	

<sup>a</sup> See footnotes at bottom of Table IV.

Table VII.. Results for Calcium, Stronium, and Barium Nitrates  
in Synthetic Mixtures

<u>Added (grams)</u>		<u>Found (grams)</u>	
<u>Ca(NO<sub>3</sub>)<sub>2</sub></u>	<u>Ba(NO<sub>3</sub>)<sub>2</sub></u>	<u>Ca(NO<sub>3</sub>)<sub>2</sub></u>	<u>Ba(NO<sub>3</sub>)<sub>2</sub></u>
0.0749	0.2332	0.0765	0.2316
0.0508	0.0517	0.0496	0.0515
0.0120	0.1009	0.0120	0.1004
0.0055	0.0049	0.0053	0.0046
0.0010	0.0015	0.0009	0.0013
<u>Ca(NO<sub>3</sub>)<sub>2</sub></u>	<u>Sr(NO<sub>3</sub>)<sub>2</sub></u>	<u>Ca(NO<sub>3</sub>)<sub>2</sub></u>	<u>Sr(NO<sub>3</sub>)<sub>2</sub></u>
0.0768	0.2301	0.0755	0.2297
0.0610	0.0521	0.0610	0.0519
0.0105	0.1010	0.0110	0.1005
0.0077	0.0054	0.0071	0.0051
0.0017	0.0014	0.0015	0.0010

Table VII. Results for Lithium, Strontium, and Barium Nitrates  
in Synthetic Mixtures

<u>Added (grams)</u>		<u>Found (grams)</u>	
<u>LiNO<sub>3</sub></u>	<u>Sr(NO<sub>3</sub>)<sub>2</sub></u>	<u>LiNO<sub>3</sub></u>	<u>Sr(NO<sub>3</sub>)<sub>2</sub></u>
0.0799	0.2102	0.0792	0.2099
0.0576	0.0510	0.0550	0.0516
0.0111	0.0165	0.0111	0.0153
0.0055	0.0057	0.0056	0.0055
0.0024	0.0026	0.0022	0.0023
<u>LiNO<sub>3</sub></u>	<u>Ba(NO<sub>3</sub>)<sub>2</sub></u>	<u>LiNO<sub>3</sub></u>	<u>Ba(NO<sub>3</sub>)<sub>2</sub></u>
0.0774	0.2009	0.0762	0.2014
0.0598	0.0570	0.0576	0.0557
0.0126	0.0121	0.0115	0.0116
0.0043	0.0059	0.0041	0.0054
0.0034	0.0022	0.0035	0.0020

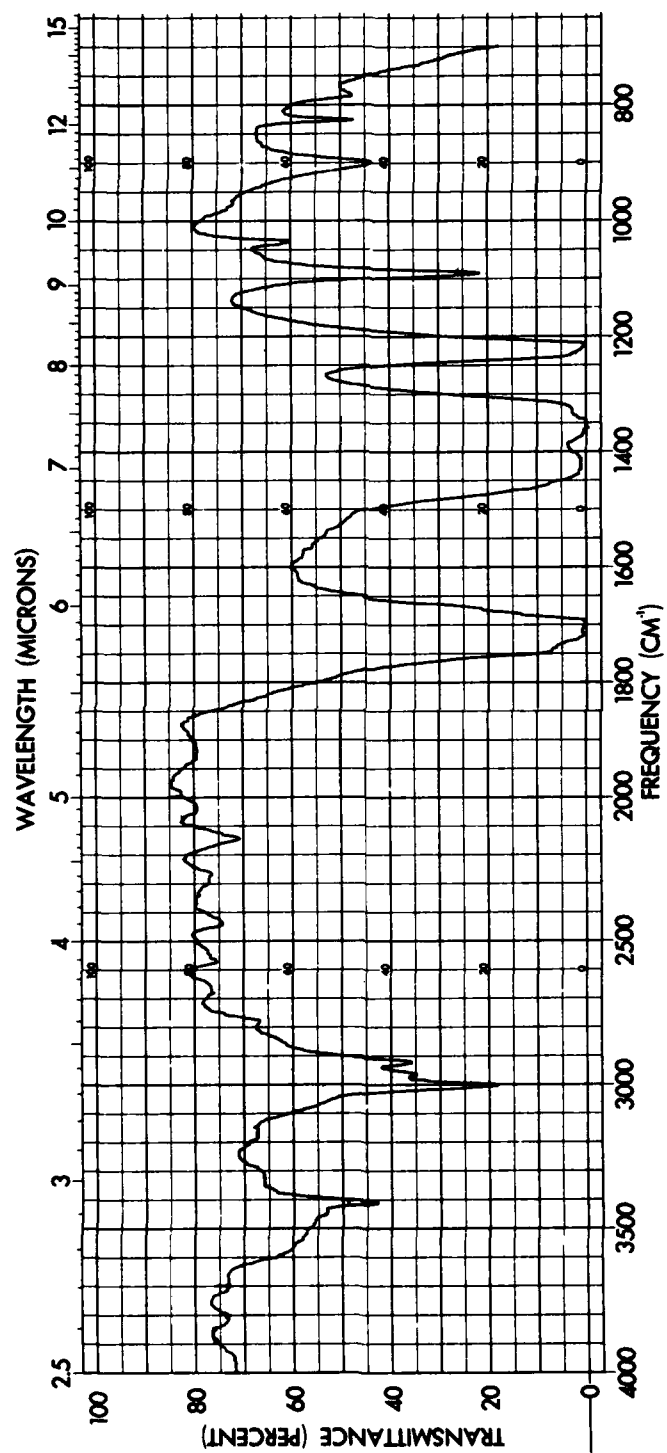


Figure 1. Infrared spectrum of  $\text{LiNO}_3$  in acetone (Irtran cell)

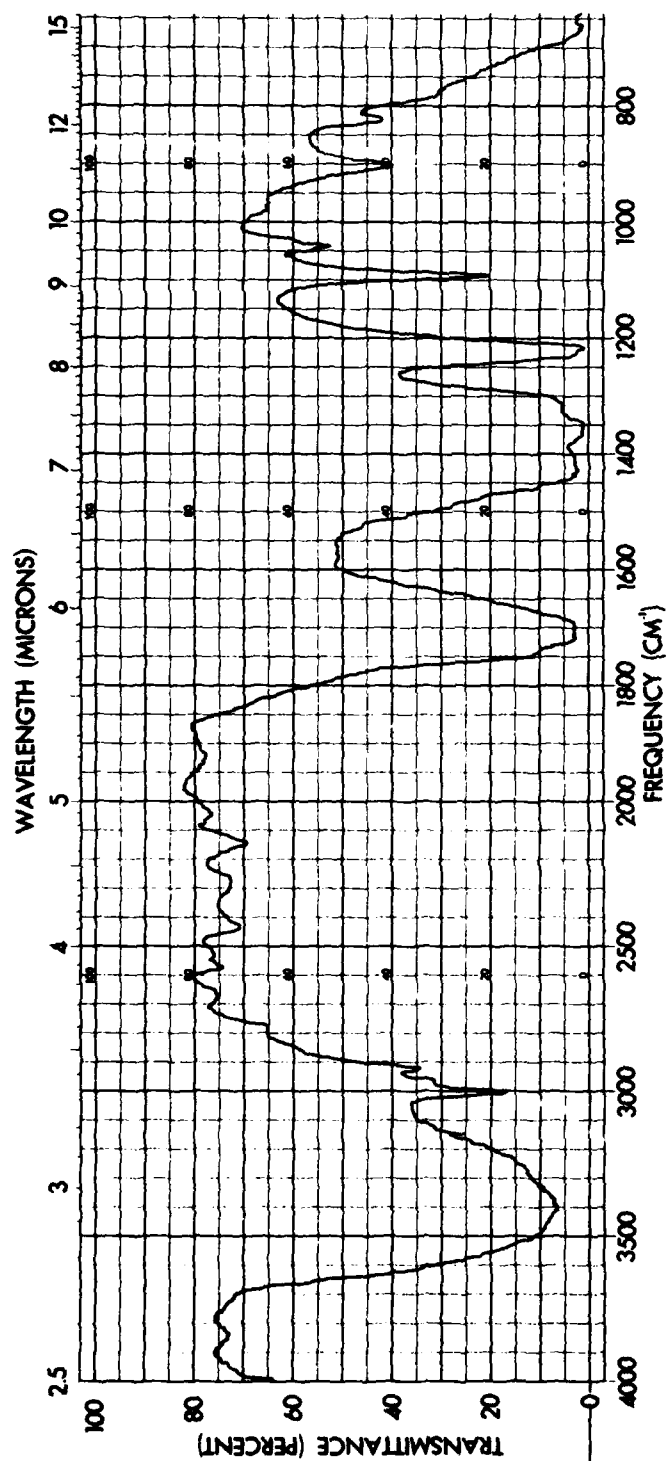


Figure 2. Infrared spectrum of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in acetone (Irtran cell)



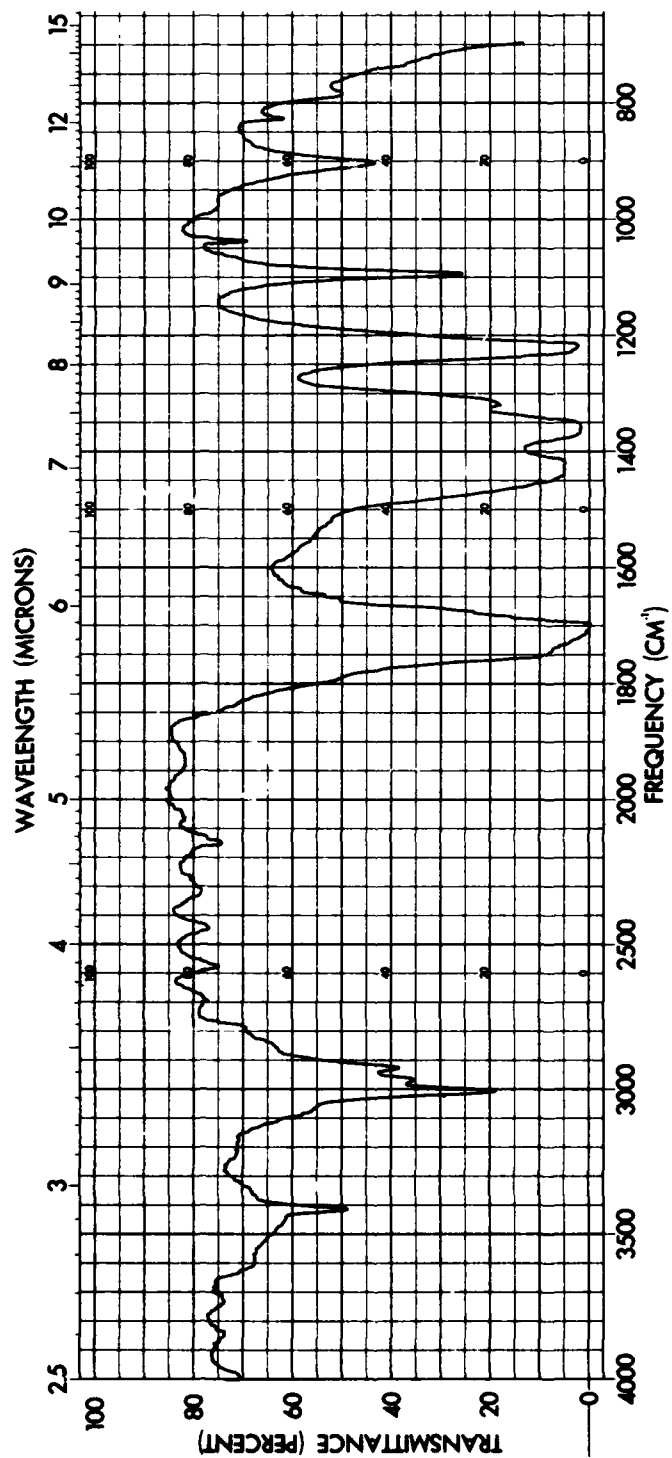


Figure 3. Infrared spectrum of  $\text{Ca}(\text{NO}_3)_2$  in acetone (Irtran cell)

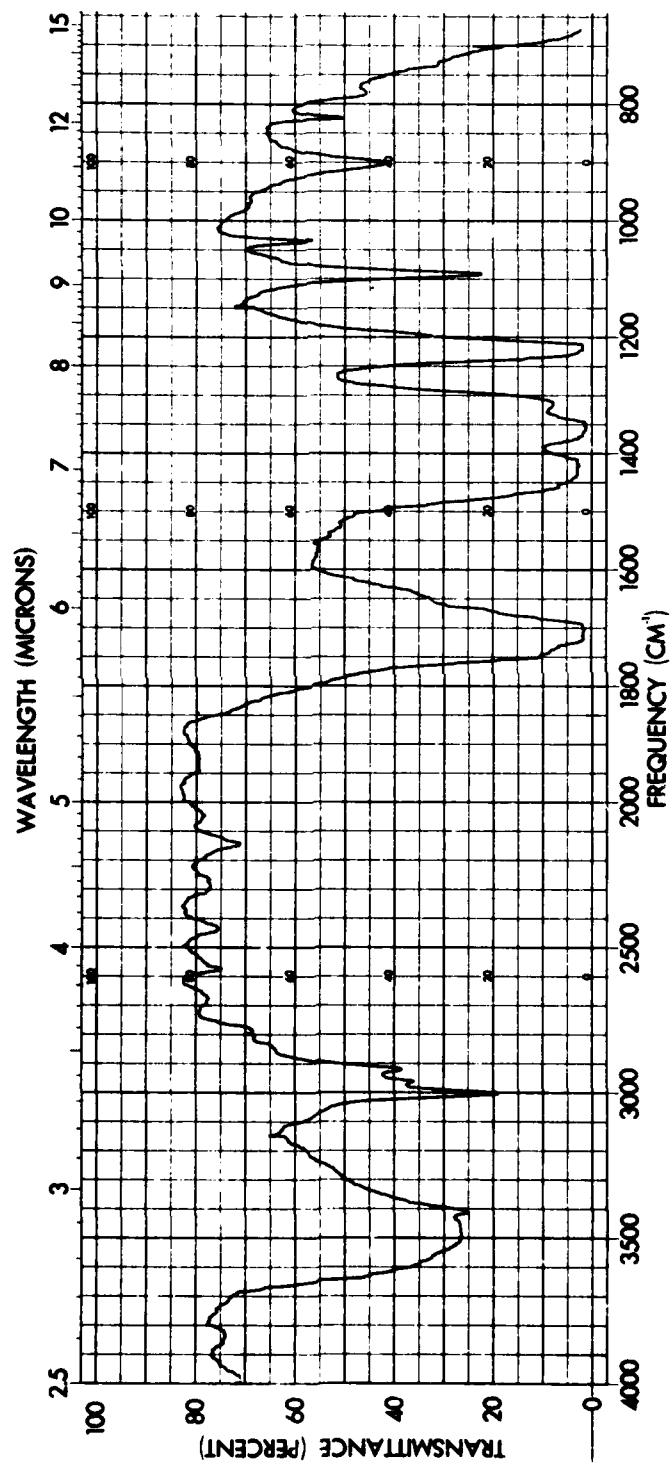


Figure 4. Infrared spectrum of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in acetone (Irtran cell)

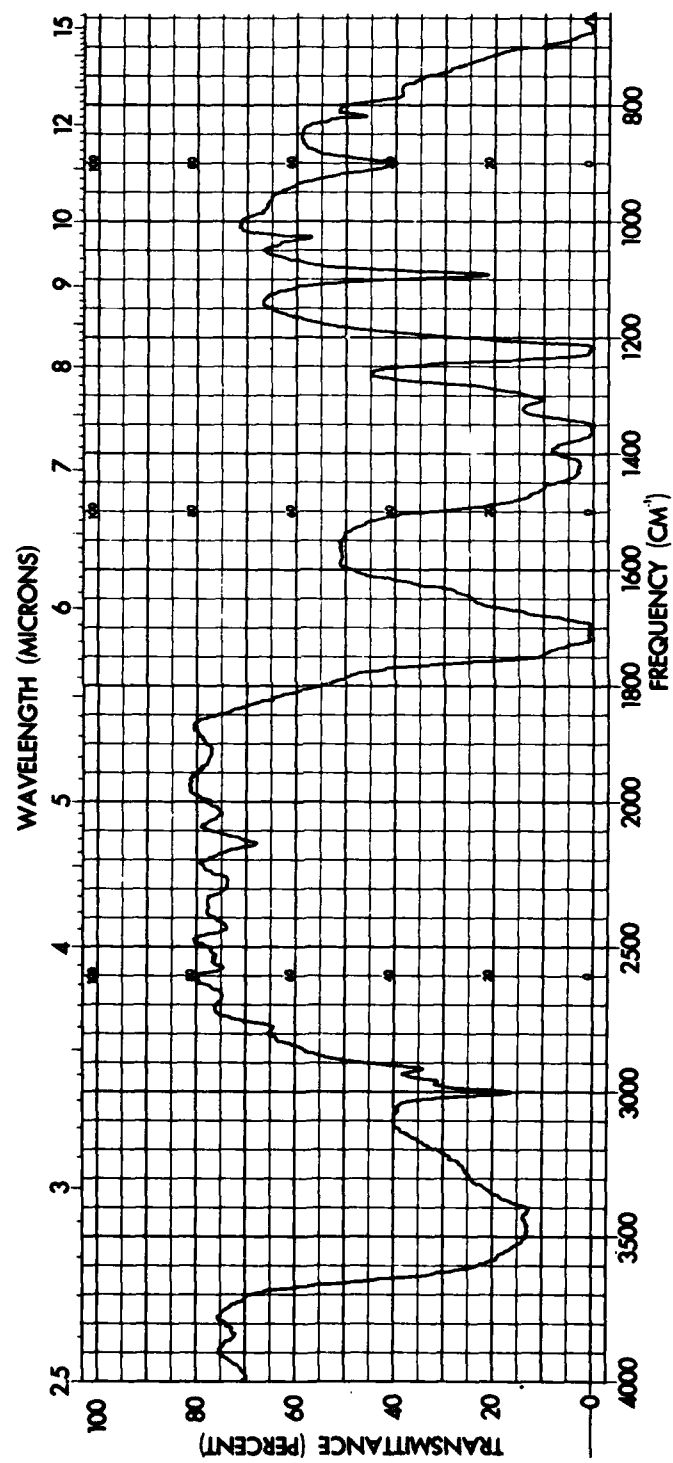


Figure 5. Infrared spectrum of  $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  in acetone (Irtran cell)

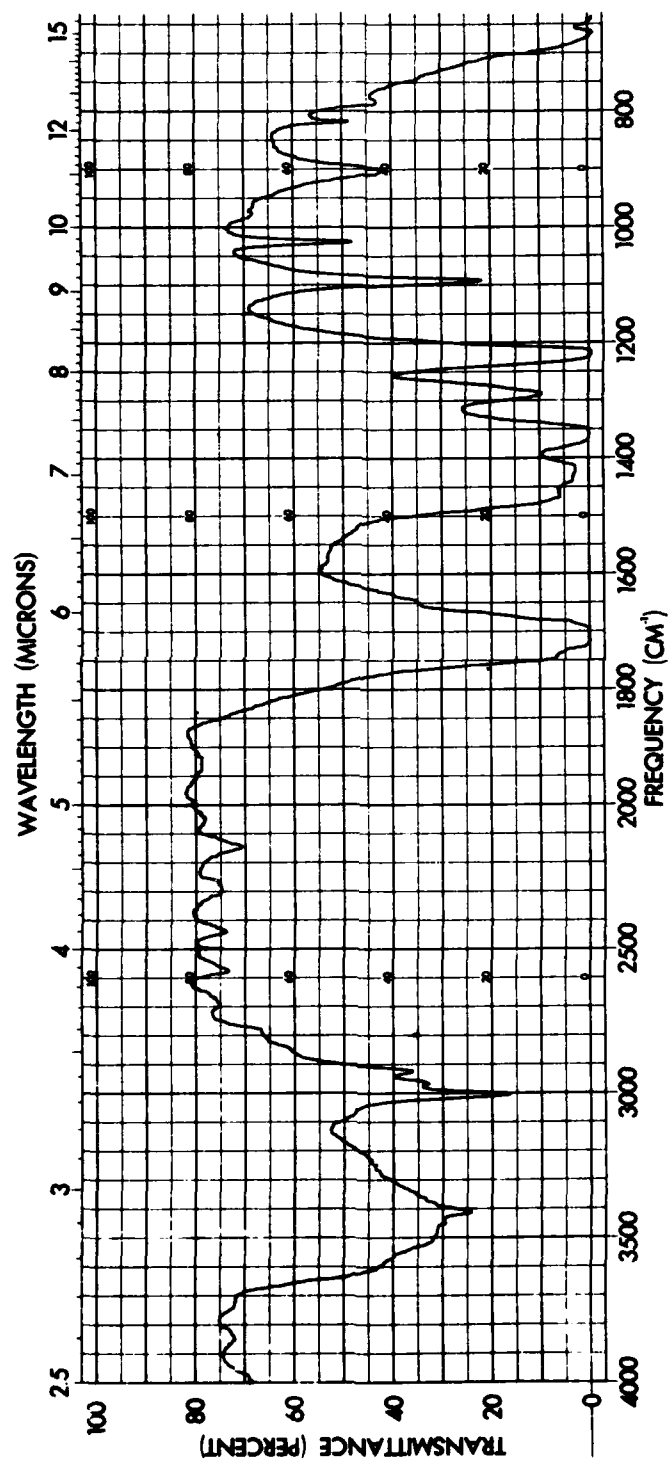


Figure 6. Infrared spectrum of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in acetone (Irtran cell)

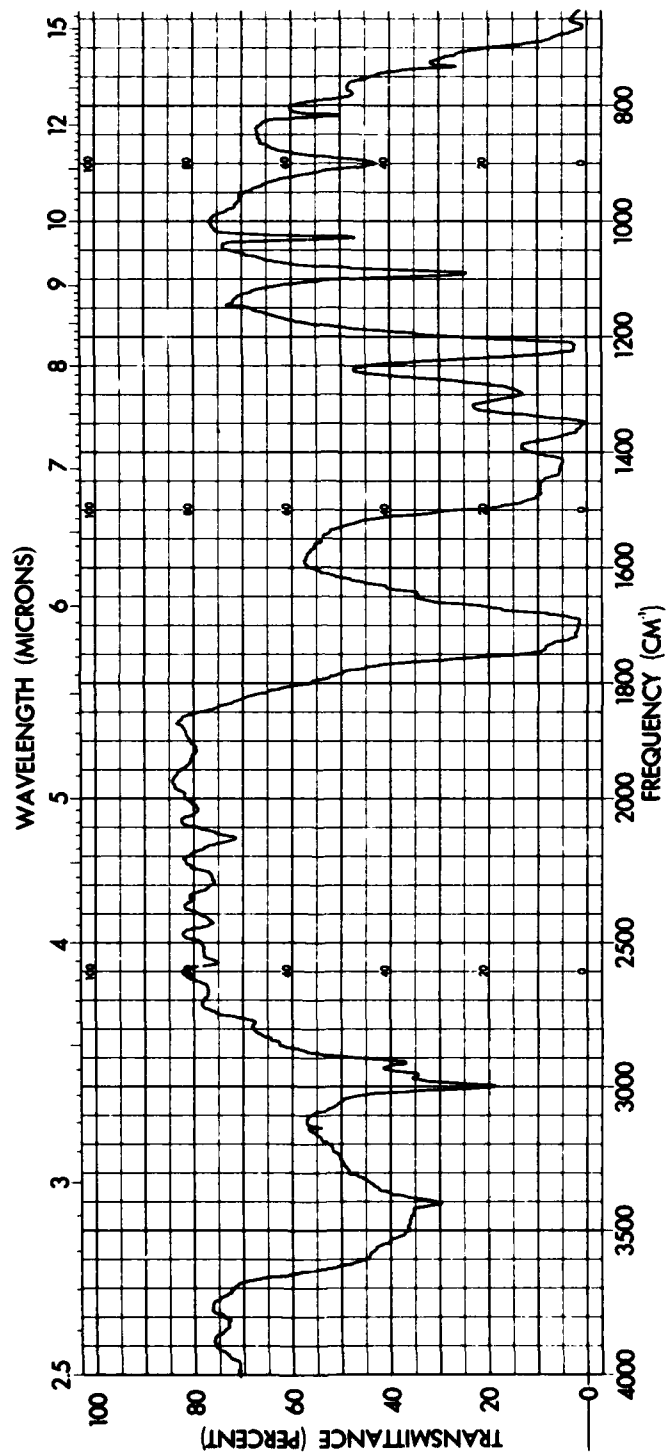


Figure 7. Infrared spectrum of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in acetone (Irtran cell)

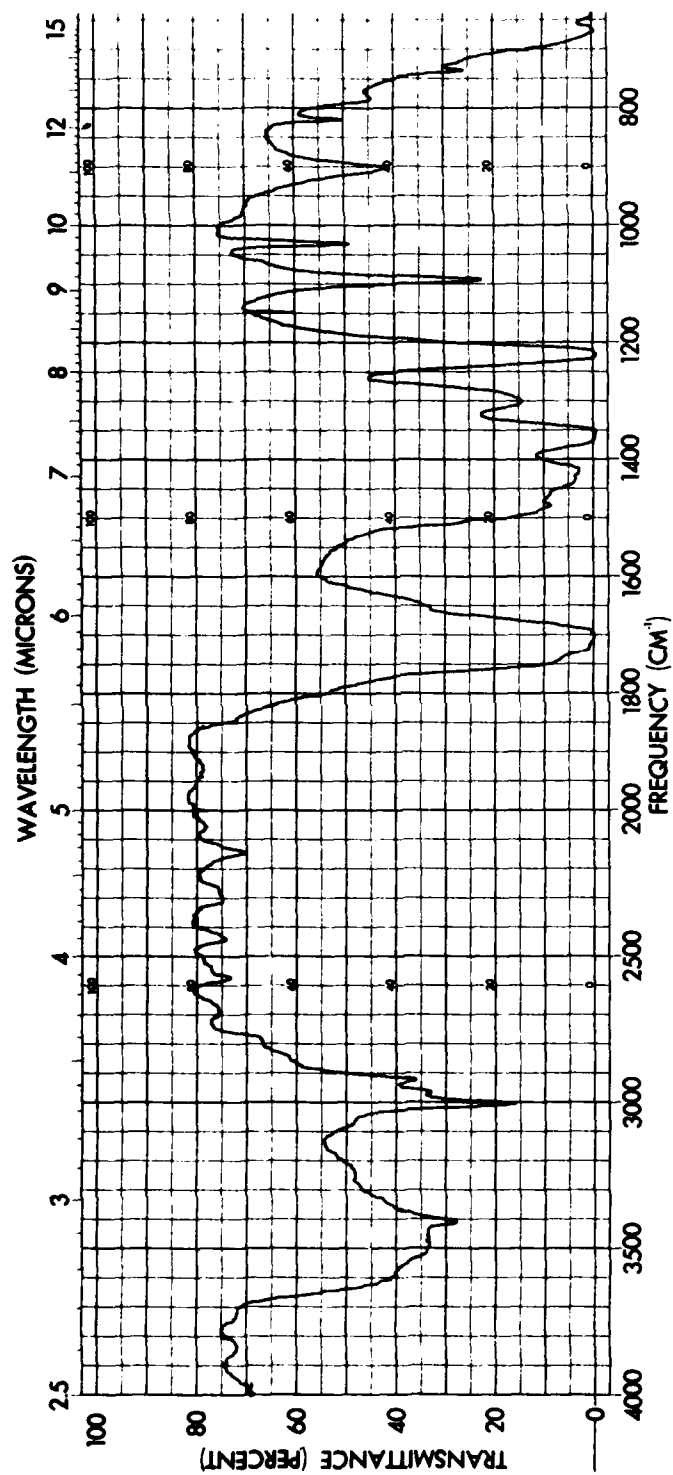


Figure 8. Infrared spectrum of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in acetone (Irtran cell)

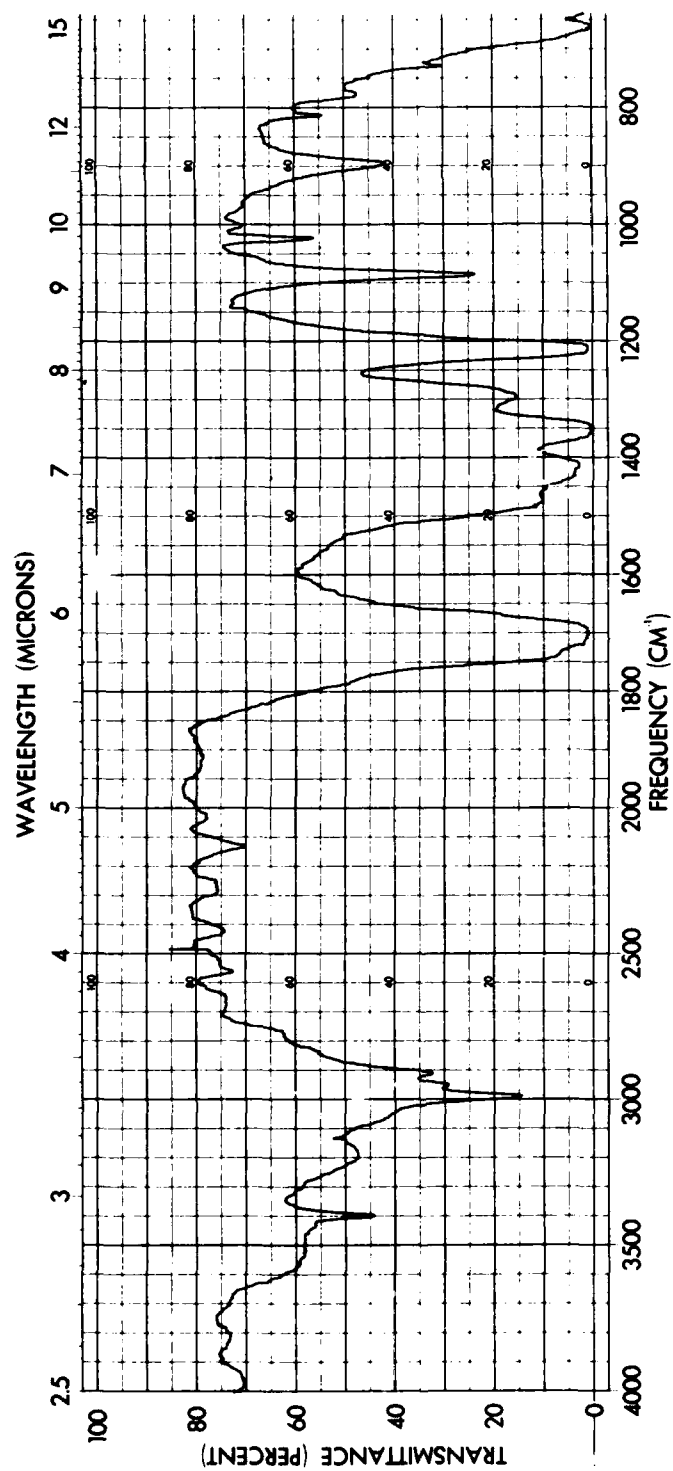


Figure 9. Infrared spectrum of  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  in acetone (Irtran cell)

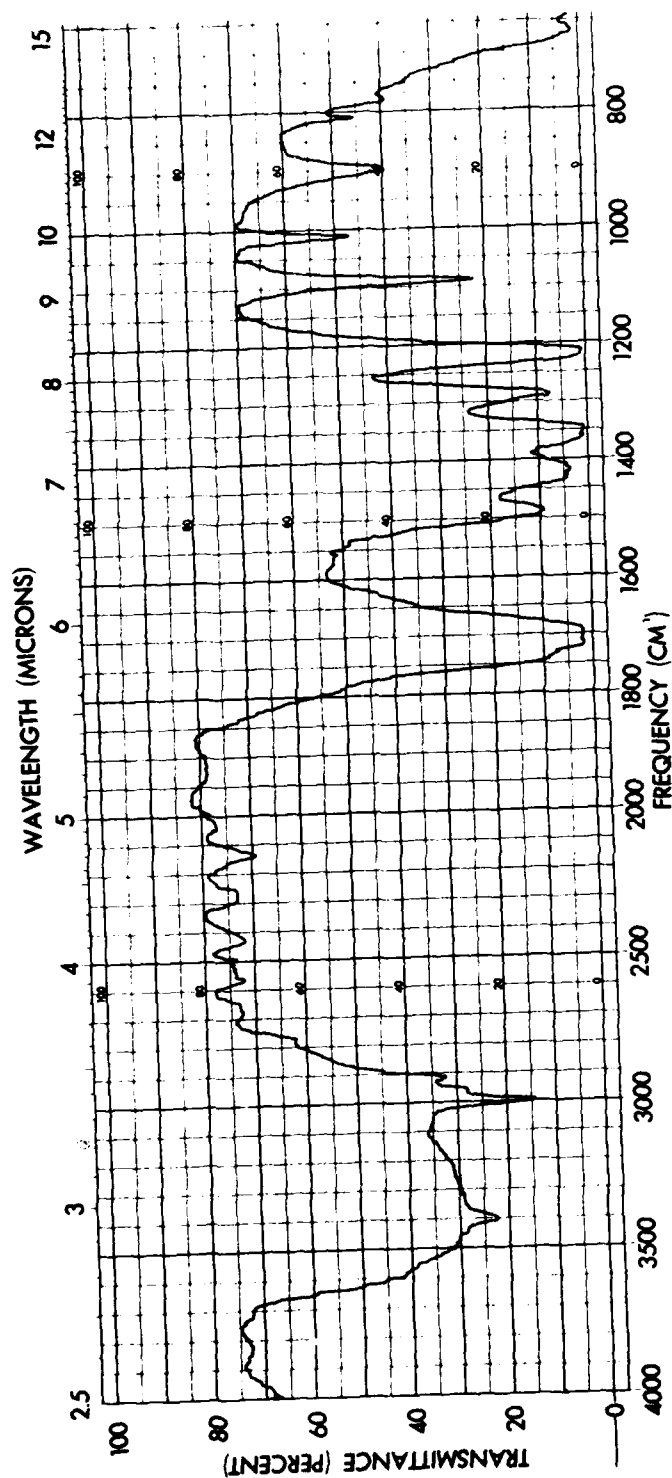


Figure 10. Infrared spectrum of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in acetone (Irtran cell)



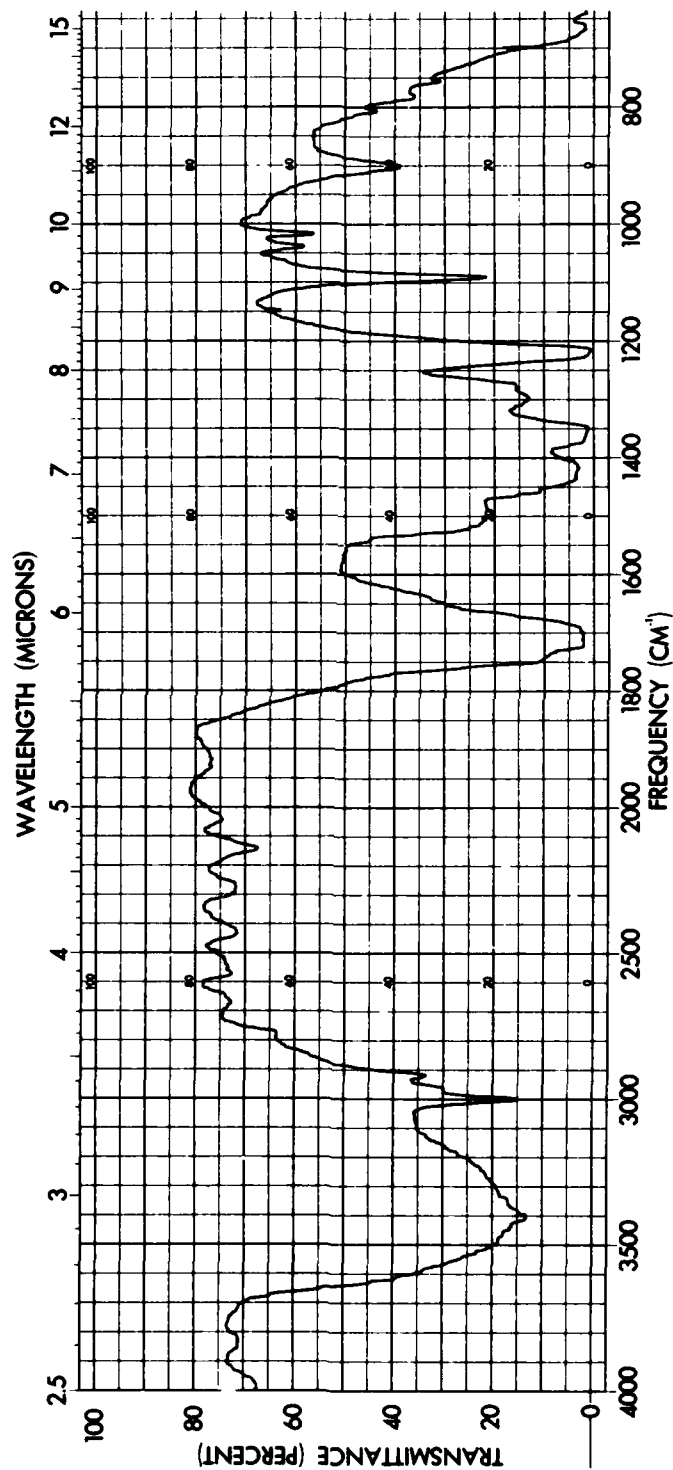


Figure 11. Infrared spectrum of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in acetone (Irtran cell)

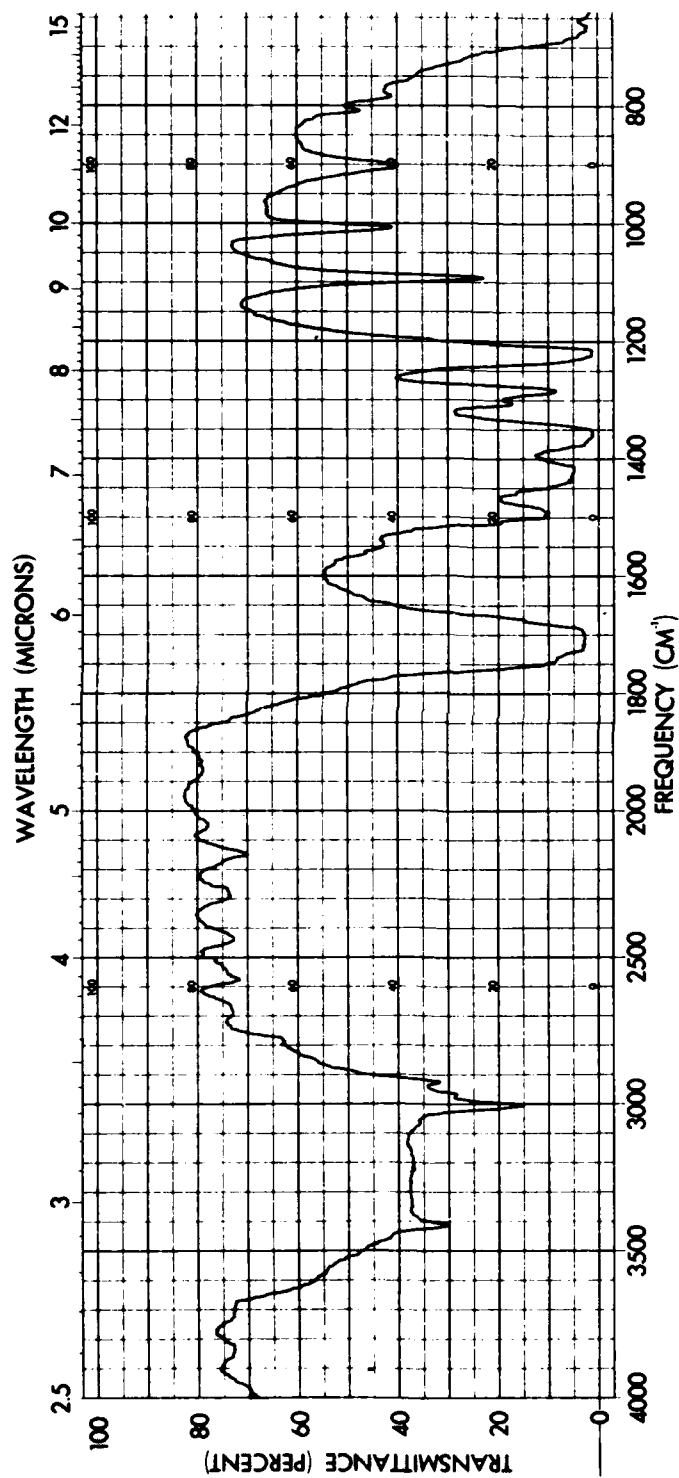


Figure 12. Infrared spectrum of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in acetone (Irtran cell)



**Figure 13. Infrared spectrum of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in acetone (Irtran cell)**

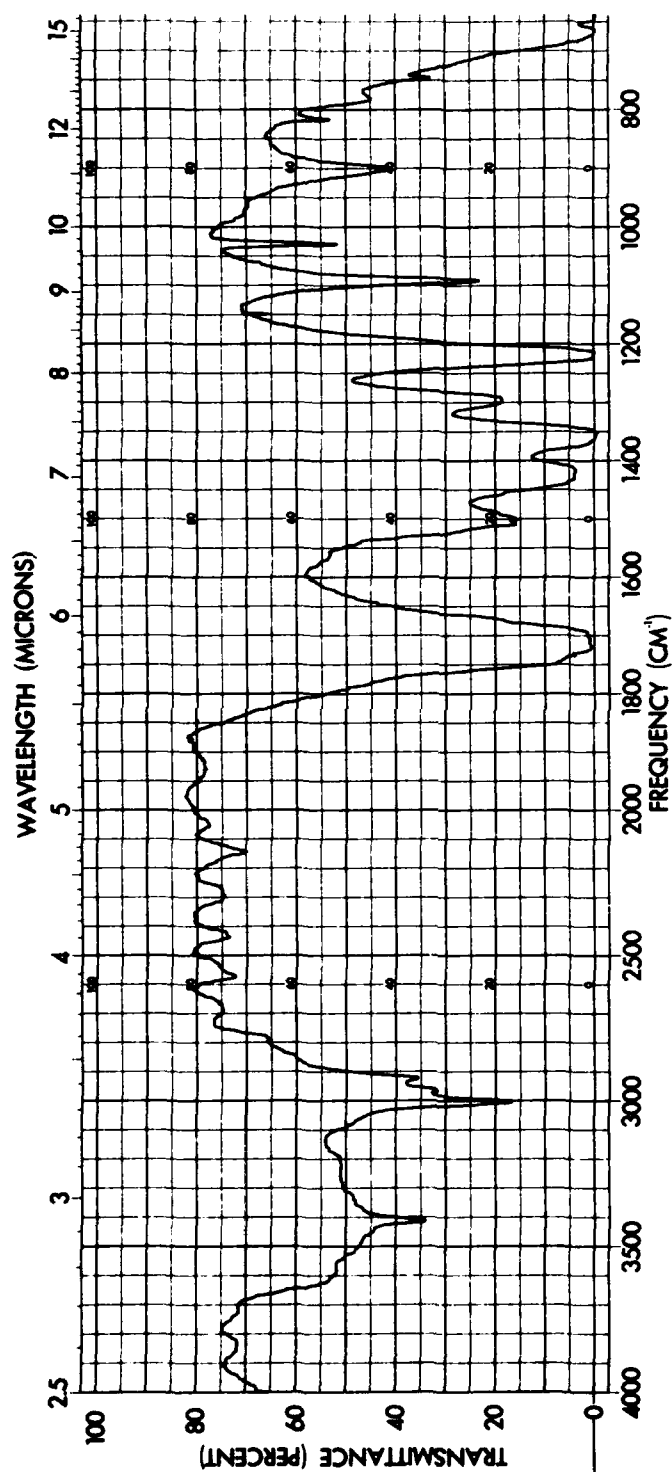


Figure 14. Infrared spectrum of  $\text{Y}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in acetone (Irtran cell)

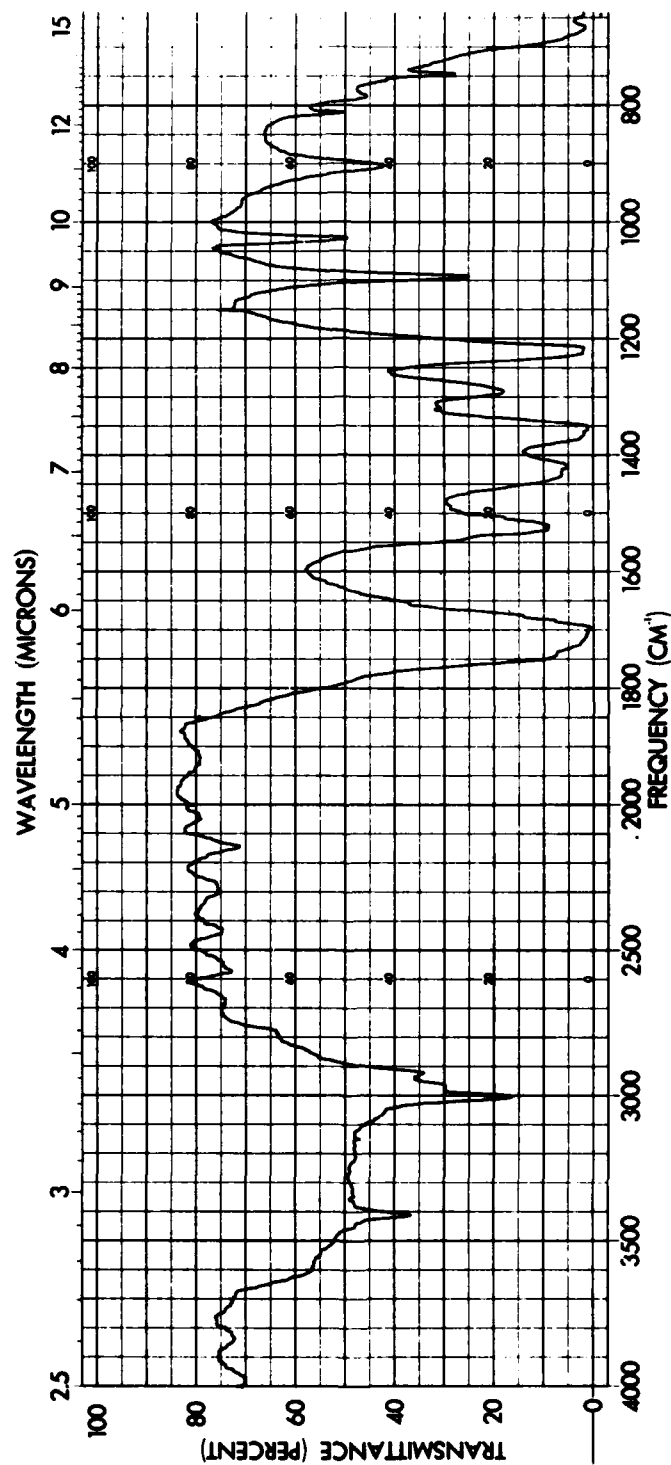


Figure 15. Infrared spectrum of  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  in acetone (Irtran cell)

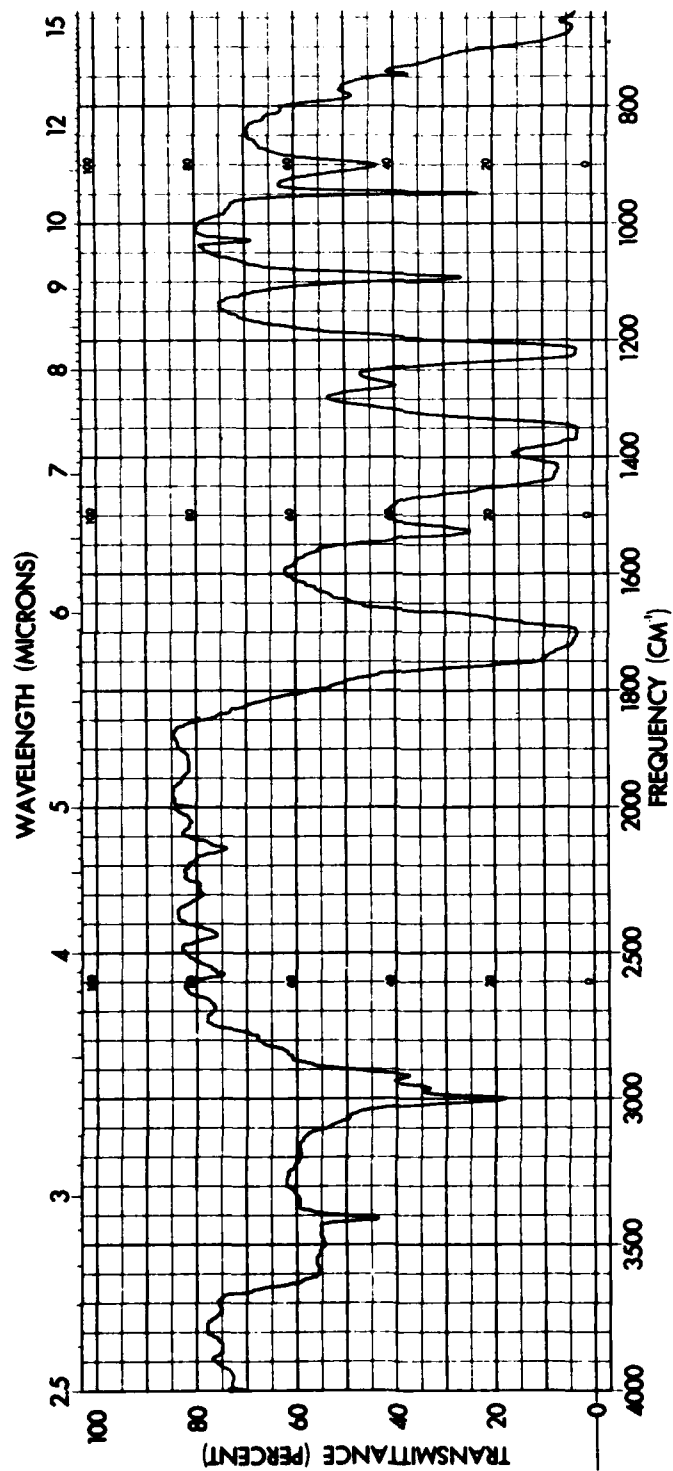


Figure 16. Infrared spectrum of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in acetone (Irtran cell)

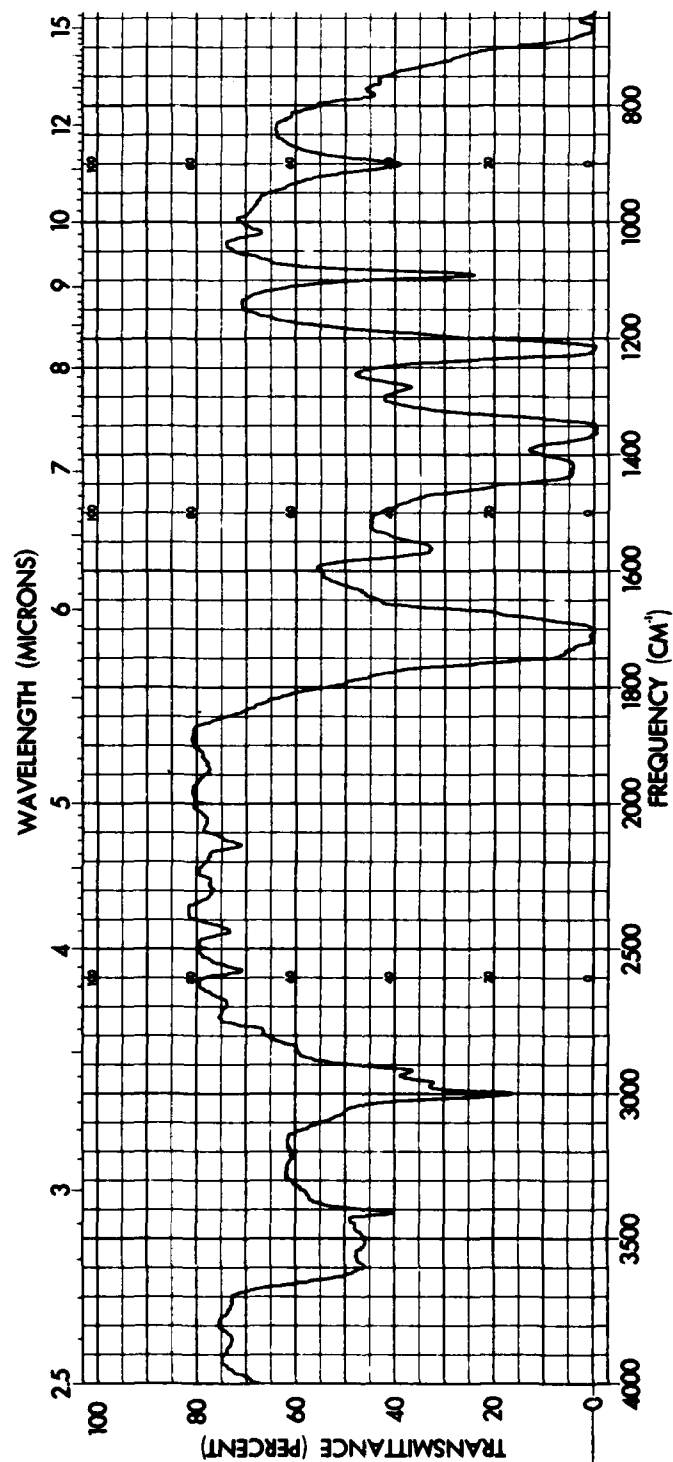


Figure 17. Infrared spectrum of  $\text{ZrO}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$  in acetone (Irtran cell)

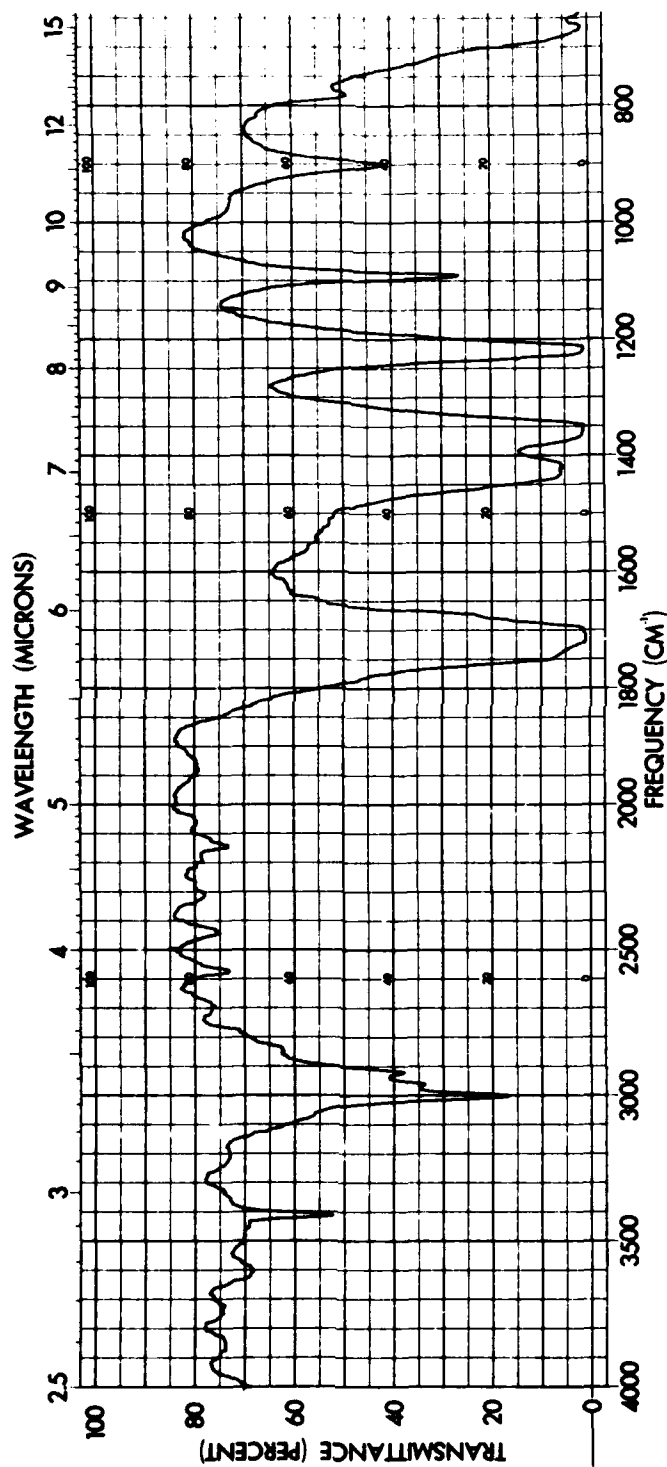


Figure 18. Infrared spectrum of acetone (Irtan cell)



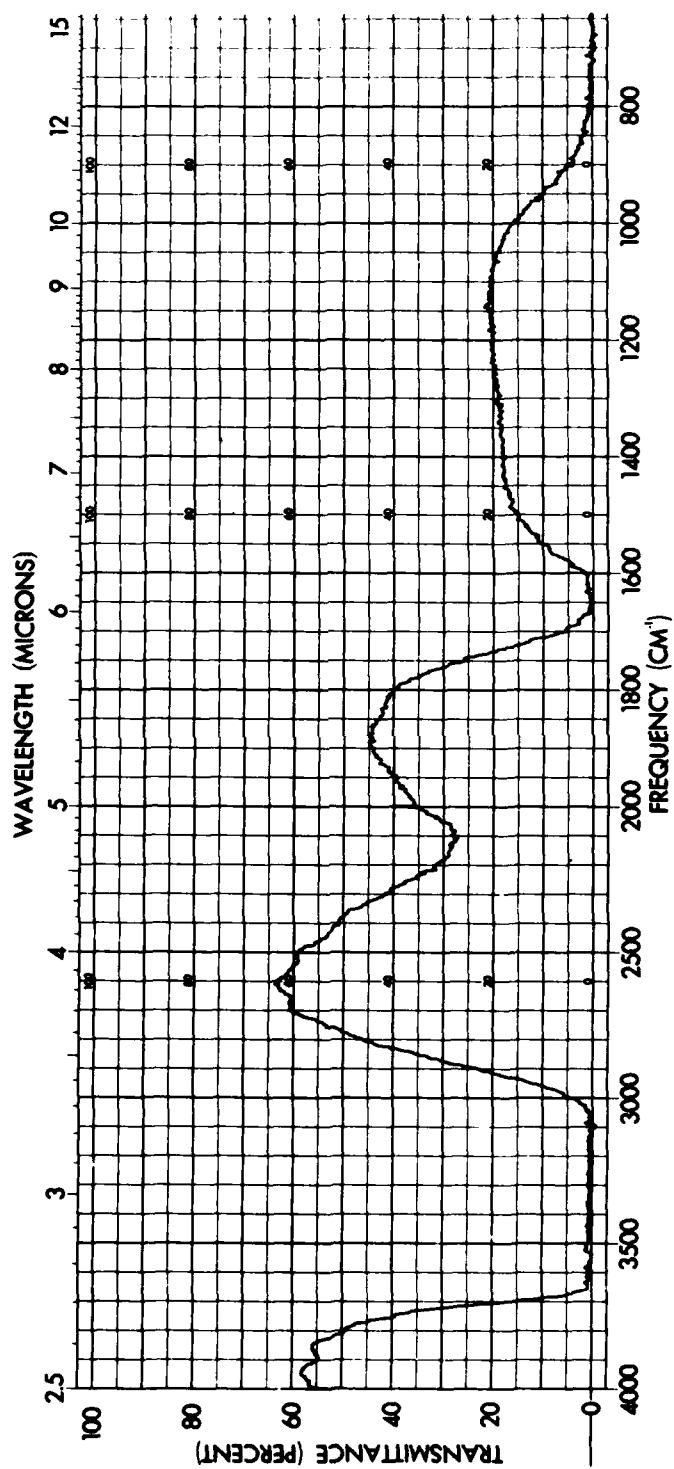


Figure 19. Infrared spectrum of water (Irtran cell)

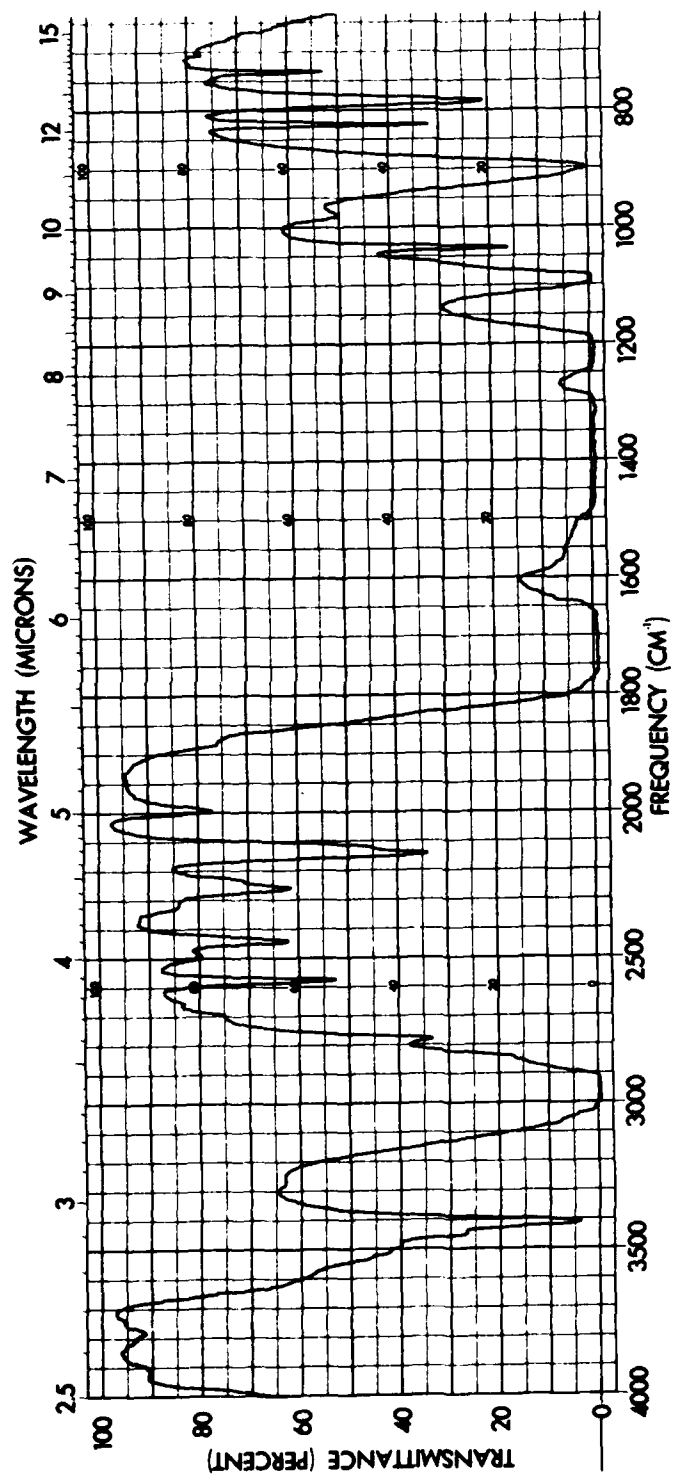


Figure 20. Infrared spectrum of  $\text{Ca}(\text{NO}_3)_2$  in acetone (sodium chloride cell)

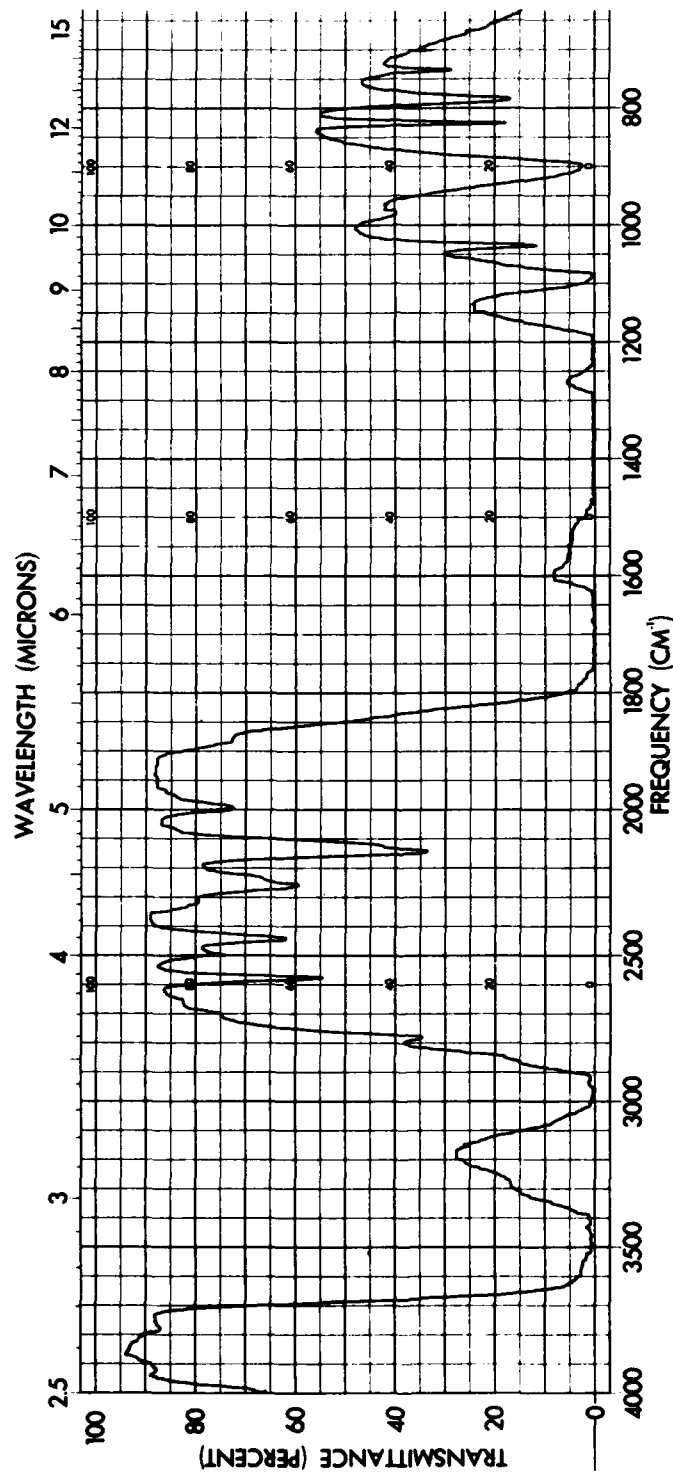


Figure 21. Infrared spectrum of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in acetone (sodium chloride cell)

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<p>A study was made of the spectra of soluble inorganic nitrates in acetone solution and the use of such spectra in analytical chemistry. The spectra of the soluble nitrates indicate the nitrate peaks in acetone can best be accommodated by a <math>C_{2v}</math> point group assignment and the nitrate groups in the nitrate acetone system are essentially covalent in character. As judged by the difference between the pair of <math>NO_2</math> stretches, <math>\nu_4</math> and <math>\nu_1</math>, the compounds tested could be classified into four groups: group 1 consisting of <math>LiNO_3</math>, <math>Mg(NO_3)_2 \cdot 6H_2O</math>, <math>Ca(NO_3)_2</math>, and <math>Ca(NO_3)_2 \cdot 4H_2O</math> which exhibited the least covalent characteristics; group 2 consisting of <math>Mn(NO_3)_2 \cdot xH_2O</math>, <math>Cd(NO_3)_2 \cdot 4H_2O</math>, <math>La(NO_3)_3 \cdot 6H_2O</math>, <math>Ce(NO_3)_3 \cdot 6H_2O</math>, and <math>(NH_4)_2Ce(NO_3)_6</math> which showed a higher degree of covalency than group 1; group 3 consisting of <math>Zn(NO_3)_2 \cdot 6H_2O</math>, <math>Ni(NO_3)_2 \cdot 6H_2O</math>, <math>Cu(NO_3)_2 \cdot 3H_2O</math>, <math>Co(NO_3)_2 \cdot 6H_2O</math>, and <math>Y(NO_3)_3 \cdot 4H_2O</math> which showed a higher degree of covalency than group 2; group 4 consisting of <math>UO_2(NO_3)_2 \cdot 6H_2O</math>, <math>Th(NO_3)_4 \cdot 4H_2O</math>, and <math>ZrO(NO_3)_3 \cdot 4H_2O</math> which showed the highest degree of covalency of all the compounds tested.</p> <p>The effect of nitrate on the acetone peaks is briefly discussed.</p> <p>A study was made of the solubilities of anhydrous inorganic nitrates in acetone. The applications of the spectra of inorganic nitrates in acetone to analytical chemistry is discussed. A method is proposed for the determination of calcium in the presence of strontium or barium by treating the nitrates with acetone, filtering off the insoluble strontium or barium nitrates, and measuring the nitrate peak from the calcium nitrate at <math>824/cm^{-1}</math>. A similar procedure is also recommended for the determination of lithium in the presence of strontium and barium.</p>			

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